PATENT ABSTRACTS OF JAPAN

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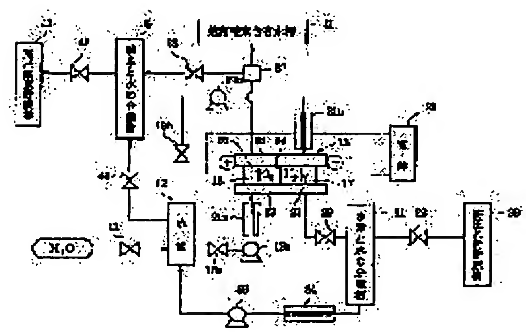
(54) PRODUCTION OF HIGH-PRESSURE GASEOUS HYDROGEN

(57)Abstract:
PROBLEM TO BE SOLVED: To make it possible to suppress liquid resistance without adding a large amt. of electrolyte and to easily produce gaseous hydrogen of a high pressure with high electrolytic efficiency.
SOLUTION: Water is supplied to an anode chamber 16 and cathode chamber 17, respectively, which are partitioned by an insulative diaphragm 14 which is permeable to H+ ions and OH− ions but have poor air permeability. An electrolysis is effected by maintaining the water of the anode chamber 16 and the cathode chamber 17 in a subcritical state and superctritical state, respectively. Either or both of the pressure or temp. of the water contg. the gaseous hydrogen in the subcritical state or superctritical state generated in the anode chamber 17 is lowered, by which the gaseous hydrogen of the high pressure is taken out.



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CLAIMS

[Claim(s)]
[Claim 1] The process which supplies water to the anode plate room (16) divided with the insulating diaphragm with scarce permeability (14), and a cathode room (17), respectively although H+ ion and OH-ion are penetrated, The process which electrolyzes by changing the water of said anode plate room (16) and a cathode room (17) into a subcritical state or a supercritical condition, respectively, The manufacture approach of high-pressure hydrogen gas including the process which takes out high-pressure hydrogen gas by reducing either or the both sides of the pressure of the water containing the hydrogen gas of the subcritical state produced at said cathode room (17), or a supercritical condition, or temperature.
[Claim 2] The manufacture approach of the high-pressure hydrogen gas according to claim 1 added to the water supplied to an anode plate room (16) and a cathode room (17) after cooling the residual liquor which took out high-pressure hydrogen gas.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the approach of electrolyzing the water of a subcritical state or a supercritical condition, and manufacturing high-pressure hydrogen gas.
[0002]
[Description of the Prior Art] Manufacture of the hydrogen by electrolysis is performed for many years. room temperature [after adding a lot of electrolytes (for example, number - alkali, such as dozens of% of sodium hydroxide and a potassium hydroxide) in water in order to raise the conductivity of water in a conventional method since conductivity is bad when electrolyzing water] - 100 -- it energizes by the pressure of the temperature of dozens of degrees C, and ordinary pressure - 10 atmospheric pressure, and hydrogen gas is manufactured.
[0003]
[Problem(s) to be Solved by the Invention] However, by the above-mentioned conventional approach, the hydrogen gas generated by electrolysis exists as air bubbles in underwater and an electrode surface, and has the problem on which these air bubbles increase liquid resistance (electric resistance value of a liquid), and reduce electrolysis effectiveness. Moreover, since it is necessary to add a lot of electrolytes, there is un-arranging [for which a manufacturing cost increases]. Furthermore, to manufacture high-pressure hydrogen gas, it is necessary to pressurize the hydrogen gas produced in electrolysis. The purpose of this invention can control liquid resistance, without adding a lot of electrolytes, and is to offer the approach of manufacturing high-pressure hydrogen gas easily at high electrolysis effectiveness.
[0004]
[Means for Solving the Problem] The process which supplies water to the anode plate room 16 divided with the insulating diaphragm 14 with scarce permeability, and the cathode room 17, respectively although invention concerning claim 1 penetrates H+ ion and OH-ion as shown in drawing 1 , The process which electrolyzes by changing the water of the anode plate room 16 and the cathode room 17 into a subcritical state or a supercritical condition, respectively, It is the manufacture approach of high-pressure hydrogen gas including the process which takes out high-pressure hydrogen gas by reducing either or the both sides of the pressure of the water containing the hydrogen gas of the subcritical state produced at the cathode room 17, or a supercritical condition, or temperature. Since the water of a subcritical state or a supercritical condition has a diffusing capacity superior to usual water and the mass transfer in an electrode surface happens promptly, the hydrogen gas generated in the electrode surface of the cathode room 17 forms promptly the water and the homogeneity phase which are the electrolytic solution. Consequently, the amount of air bubbles of the hydrogen gas generated in the amount of air bubbles of the hydrogen gas generated in the above-mentioned electrode surface and the electrolytic solution falls, and liquid resistance is controlled. Moreover, since a reaction rate becomes large according to an elevated temperature, electrolysis effectiveness improves. Furthermore, high-pressure hydrogen gas is obtained after electrolysis, without establishing a special pressurization means.
[0005] Invention concerning claim 2 is invention concerning claim 1, and after it cools the

residual liquor which took out high-pressure hydrogen gas, it is the manufacture approach of the high-pressure hydrogen gas added to the water supplied to the anode plate room 16 and the cathode room 17. The residual liquor which took out high-pressure hydrogen gas is reused as some electrolytic solutions.

[0006]

[Embodiment of the Invention] In this invention, the subcritical state of water means the condition of the water which is 200-374 degrees C in temperature, and is in the pressure of 160-215kg/cm2. Moreover, the supercritical condition of water means the condition of the water which is 374-400 degrees C in temperature, and is in the pressure of 215-300kg/cm2. A reaction is slow and electrolysis effectiveness is not good at under the lower limit of the temperature in a subcritical state, and a pressure. Moreover, if the upper limit of the temperature in a supercritical condition and a pressure is exceeded, a load is applied to a reaction container too much, and this is not efficient, either.

[0007] When enforcing the manufacture approach of the high-pressure hydrogen gas of this invention, equipment as shown in drawing 1 is used. Water (H2O) is first supplied to a tank 12 through a bulb 11. The water stored in this tank 12 is supplied to the reaction container 13. The reaction container 13 has the anode plate room 16 and the cathode room 17 which were divided by the insulating diaphragm 14. The water of a tank 12 is specifically pressurized by the anode plate room 16 of the reaction container 13 by pump 19a through bulb 18a, and it is heated by pre-heater 21a, and it will be in a subcritical state or a supercritical condition, and will be fed. On the other hand, the water of a tank 12 is pressurized by the cathode room 17 by pump 19b through bulb 18b, and it is heated by pre-heater 21b, and it will be in a subcritical state or a supercritical condition, and will be fed. The heater 23 which heats the water in the anode plate room 16 and the cathode room 17 is formed in the perimeter of the reaction container 13, and, as for water, this maintains a subcritical state or a supercritical condition in the reaction container 13. The cathode 27 inserted in the anode plate 26 and the cathode room 17 which were inserted in the anode plate room 16 is connected to a power source 28, respectively.

[0008] As an ingredient of the electrode which constitutes this anode plate 26 and cathode 27, a metal, solid electrolytes, etc., such as platinum, titanium, a tantalum, and an iron system, can be used. The configuration of a plate, a rod, a network, etc. is sufficient as the configuration of an electrode. Moreover, since supercritical water has the diffusing power superior to usual water, when a porous electrode is used, it has the advantage which breadth reaction effectiveness increases [the effective reaction surface area of an electrode]. Moreover, although H+ ion and OH-ion are penetrated as an insulating diaphragm 14, permeability is scarce, for example, porosity ceramics, such as a silica and an alumina, are used. Although these insulators are porous membrane which has the aperture of a micron unit and water is passed, most of the generated hydrogen gas or oxygen gas has the property which is not passed. If it energizes to an anode plate 26 and cathode 27 in this condition, as shown in a degree type, water is electrolyzed, hydrogen gas (H2 gas) will be generated at the cathode room 17, and oxygen gas (O2 gas) will generate it at the anode plate room 16, respectively. Since the anode plate room 16 and the cathode room 17 are isolated by the insulating diaphragm 14, the hydrogen gas and oxygen gas which occurred are not mixed.

[0009] a cathode room -- 17: 2OH- -> H2O + 2e -- the water containing the hydrogen gas generated at - + 1 / 2O2** cathode room 17 is picked out from the reaction container 13, and is sent to the separation tub 31 of hydrogen and water through a reducing valve 29. : 2H2O + 2e- -> 2OH- + H2** anode plate room 16 Here, it separates into water and high-pressure hydrogen gas by descending a pressure with a reducing valve 29. The separated high-pressure hydrogen gas is sent and saved through a bulb 32 at the high-pressure hydrogen storage tank 33. After being cooled with a condensator 34, the water separated from hydrogen gas by the separation tub 31 of hydrogen and water is pressurized with a pump 36, is collected by the tank 12, and is reused as the electrolytic solution of the reaction container 13.

[0010] It is taken out from the reaction container 13, on the other hand, a distributing valve 37 reaches, and the water which, on the other hand, contains the oxygen gas which occurred at the anode plate room 16 is sent to the separation tub 39 of oxygen and water through a reducing

valve 38. Here, it separates into water and oxygen gas by descending a pressure with a reducing valve 38. The water containing the oxygen gas which passed through another side of a distributing valve 37 is sent and saved in the saturation oxygen content tank 41. The saturation oxygen content water of this tank 41 is used for liquefaction of coal etc. The separated high-pressure oxygen gas is sent and saved through a bulb 42 at the high-pressure-oxygen storage tank 43, and the water separated from oxygen gas by the separation tub 39 is collected by the tank 12 through a bulb 44, and is reused as the electrolytic solution of the reaction container 13.

[0011]
[Effect of the Invention] Water is supplied to the anode plate room and cathode room which H+ ion and OH-ion were penetrated according to this invention as stated above, but were divided with the insulating diaphragm with scarce permeability, respectively. It electrolyzes by changing the water of an anode plate room and a cathode room into a subcritical state or a supercritical condition, respectively. Since high-pressure hydrogen gas was taken out by reducing either or the both sides of the pressure of the water containing the hydrogen gas of the subcritical state produced at the cathode room, or a supercritical condition, or temperature The amount of air bubbles of the hydrogen gas generated in the amount of air bubbles of the hydrogen gas generated in an electrode surface and the electrolytic solution falls, and liquid resistance is controlled. Moreover, electrolysis effectiveness can be raised, without adding a lot of electrolytes like a conventional method. Moreover, high-pressure hydrogen gas is obtained, without establishing the pressurization means by which it is special after electrolysis.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The block diagram of the manufacturing installation of the high-pressure hydrogen gas of this invention.
[Description of Notations]
14 Insulating Diaphragm
16 Anode Plate Room
17 Cathode Room

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DOCUMENT 1/1
DOCUMENT NUMBER
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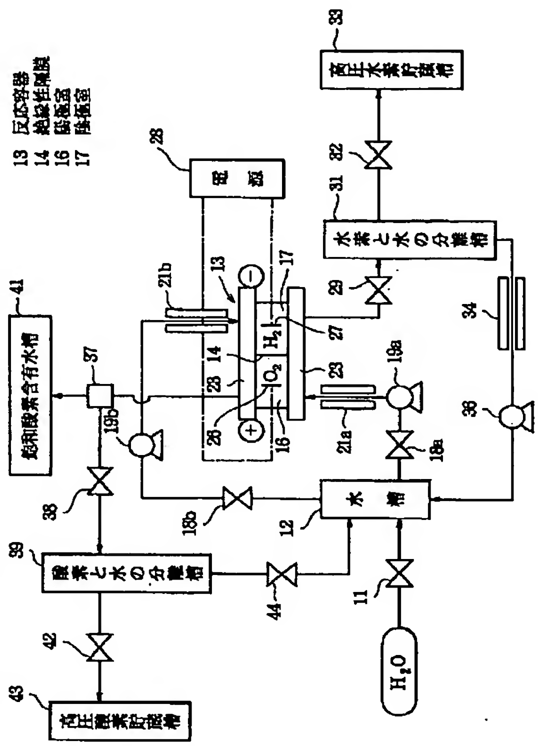
1. JP,11-279782,A(1999)

Drawing selection Representative drawing



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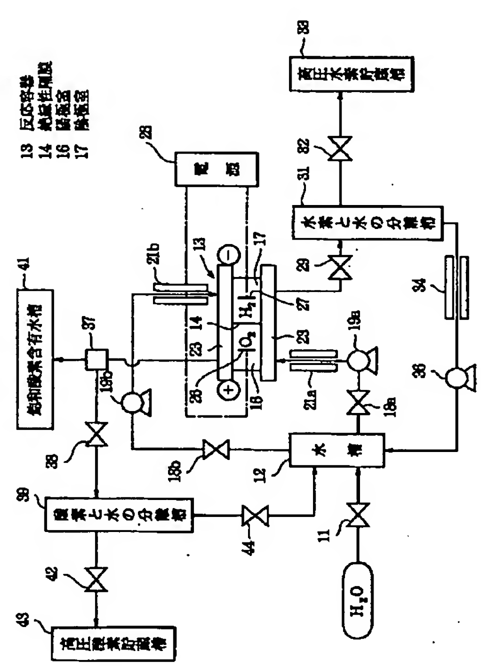
(54)【発明の名称】　高圧水素ガスの製造方法

(57)【要約】

【課題】　多量の電解質を添加せずに液抵抗を抑制することができ、高い電解効率で容易に高圧の水素ガスを製造する。

【解決手段】　H^+イオン及びOH^-イオンを透過するが通気性の乏しい絶縁性隔膜１４で仕切られた陽極室１６と陰極室１７にそれぞれ水を供給する。陽極室１６及び陰極室１７の水をそれぞれ亜臨界状態又は超臨界状態にして電気分解を行う。陰極室１７で生じた亜臨界状態又は超臨界状態の水素ガスとを含む水の圧力又は温度のいずれか一方又は双方を低下させることにより高圧の水素ガスを取出す。



【特許請求の範囲】

【請求項１】　H^+イオン及びOH^-イオンを透過するが通気性の乏しい絶縁性隔膜(14)で仕切られた陽極室(16)と陰極室(17)にそれぞれ水を供給する工程と、
前記陽極室(16)及び陰極室(17)の水をそれぞれ亜臨界状態又は超臨界状態にして電気分解を行う工程と、
前記陰極室(17)で生じた亜臨界状態又は超臨界状態の水素ガスを含む水の圧力又は温度のいずれか一方又は双方を低下させることにより高圧の水素ガスを取出す工程とを含む高圧水素ガスの製造方法。

【請求項２】　高圧の水素ガスを取出した残液を冷却した後、陽極室(16)及び陰極室(17)に供給する水に加える請求項１記載の高圧水素ガスの製造方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は亜臨界状態又は超臨界状態の水を電気分解して高圧水素ガスを製造する方法に関するものである。

【０００２】

【従来の技術】電気分解による水素の製造は古くから行われている。水を電解する場合、導電性が悪いため、従来法では水の導電性を高めるために多量の電解質（例えば数～数十%の水酸化ナトリウム、水酸化カリウム等のアルカリ）を水に添加した後、室温～百数十℃の温度、常圧～１０気圧の圧力で通電して水素ガスを製造している。

【０００３】

【発明が解決しようとする課題】しかし、上記従来方法では電解によって発生する水素ガスは水中及び電極表面において気泡として存在し、この気泡が液抵抗（液体の電気抵抗値）を増大させて電解効率を低下させる問題がある。また多量の電解質を添加する必要があるため、製造コストが増大する不都合がある。更に高圧の水素ガスを製造する場合には、電解で生じた水素ガスを加圧する必要がある。本発明の目的は、多量の電解質を添加せずに液抵抗を抑制することができ、高い電解効率で容易に高圧の水素ガスを製造する方法を提供することにある。

【０００４】

【課題を解決するための手段】請求項１に係る発明は図１に示すように、H^+イオン及びOH^-イオンを透過するが通気性の乏しい絶縁性隔膜１４で仕切られた陽極室１６と陰極室１７にそれぞれ水を供給する工程と、陽極室１６及び陰極室１７の水をそれぞれ亜臨界状態又は超臨界状態にして電気分解を行う工程と、陰極室１７で生じた亜臨界状態又は超臨界状態の水素ガスとを含む水の圧力又は温度のいずれか一方又は双方を低下させることにより高圧の水素ガスを取出す工程とを含む高圧水素ガスの製造方法である。亜臨界状態又は超臨界状態の水は通常の水よりも優れた拡散能力を有し、電極表面での物質移動が速やかに起るため、陰極室１７の電極表面で発生

した水素ガスは速やかに電解液である水と均一相を形成する。この結果、上記電極表面で発生する水素ガスの気泡量及び電解液中で発生する水素ガスの気泡量が低下し、液抵抗が抑制される。また高温によって反応速度が大きくなるため、電解効率が向上する。更に電解後、特別の加圧手段を設けることなく高圧の水素ガスが得られる。

【０００５】請求項２に係る発明は、請求項１に係る発明であって、高圧の水素ガスを取出した残液を冷却した後、陽極室１６及び陰極室１７に供給する水に加える高圧水素ガスの製造方法である。高圧の水素ガスを取出した残液は電解液の一部として再利用される。

【０００６】

【発明の実施の形態】本発明において、水の亜臨界状態とは２００～３７４℃の温度でかつ１６０～２１５ｋｇ／ｃｍ²の圧力にある水の状態を意味する。また水の超臨界状態とは３７４～４００℃の温度でかつ２１５～３００ｋｇ／ｃｍ²の圧力にある水の状態を意味する。亜臨界状態における温度及び圧力の下限値未満では、反応が遅く、電解効率が良くない。また超臨界状態における温度及び圧力の上限値を超えると反応容器に負荷がかかり過ぎ、これも効率的でない。

【０００７】本発明の高圧水素ガスの製造方法を実施する場合には、例えば図１に示すような装置が用いられる。先ず水（H_2O）がバルブ１１を介して水槽１２に供給される。この水槽１２に貯えられた水は反応容器１３に供給される。反応容器１３は絶縁性隔膜１４により仕切られた陽極室１６と陰極室１７を有する。具体的には反応容器１３の陽極室１６には水槽１２の水がバルブ１８ａを介してポンプ１９ａで加圧され、かつプレヒータ２１ａで加熱されて亜臨界状態又は超臨界状態となって圧送される。一方陰極室１７には水槽１２の水がバルブ１８ｂを介してポンプ１９ｂで加圧され、かつプレヒータ２１ｂで加熱されて亜臨界状態又は超臨界状態となって圧送される。反応容器１３の周囲には陽極室１６及び陰極室１７内の水を加熱するヒータ２３が設けられ、これにより反応容器１３内において水は亜臨界状態又は超臨界状態を維持する。陽極室１６に挿入された陽極２６及び陰極室１７に挿入された陰極２７はそれぞれ電源２８に接続される。

【０００８】この陽極２６及び陰極２７を構成する電極の材料としては白金、チタン、タンタル、鉄系等の金属及び固体電解質等を用いることができる。電極の形状は板、棒、網等のような形状でもよい。また超臨界水は通常の水より優れた拡散能を有するため、多孔質の電極を用いた場合には電極の有効反応表面積が広がり反応効率が増加する利点がある。また絶縁性隔膜１４としてはH^+イオン及びOH^-イオンを透過するが通気性の乏しい、例えばシリカ、アルミナ等の多孔質セラミックが用いられる。これらの絶縁体はミクロン単位の孔径を有する多

孔質膜であって、水は通過させるが、生成した水素ガスや酸素ガスは殆ど通過させない性質を有する。この状態において陽極２６及び陰極２７に通電すると、次式で示すように水は電気分解されて陰極室１７では水素ガス（H_2ガス）が、陽極室１６では酸素ガス（O_2ガス）がそれぞれ発生する。陽極室１６と陰極室１７は絶縁性隔膜１４により隔離しているため、発生した水素ガスと酸素ガスが混ざり合うことはない。

【０００９】陰極室１７：　$2H_2O + 2e^- \rightarrow 2OH^- + H_2\uparrow$

陽極室１６：　$2OH^- \rightarrow H_2O + 2e^- + 1/2O_2\uparrow$

陰極室１７で発生した水素ガスを含む水は反応容器１３から取出され、減圧弁２９を介して水素と水の分離槽３１に送られる。ここでは減圧弁２９で圧力を降下することにより水と高圧の水素ガスに分離される。分離された高圧の水素ガスはバルブ３２を介して高圧水素貯蔵槽３３に送られて保存される。水素と水の分離槽３１で水素ガスから分離された水は冷却器３４で冷却された後、ポンプ３６で加圧されて水槽１２に回収され、反応容器１３の電解液として再利用される。

【００１０】一方、陽極室１６で発生した酸素ガスを含む水は反応容器１３から取出され、分配弁３７の一方及び減圧弁３８を介して酸素と水の分離槽３９に送られる。ここでは減圧弁３８で圧力を降下することにより水と酸素ガスに分離される。分配弁３７の他方を通過した酸素ガスを含む水は飽和酸素含有水槽４１に送られて保＊

＊存される。この水槽４１の飽和酸素含有水は石炭の液化などに利用される。分離された高圧の酸素ガスはバルブ４２を介して高圧酸素貯蔵槽４３に送られて保存され、分離槽３９で酸素ガスから分離された水はバルブ４４を介して水槽１２に回収され、反応容器１３の電解液として再利用される。

【００１１】

【発明の効果】以上述べたように、本発明によれば、H^+イオン及びOH^-イオンを透過するが通気性の乏しい絶縁性隔膜で仕切られた陽極室と陰極室にそれぞれ水を供給し、陽極室及び陰極室の水をそれぞれ亜臨界状態又は超臨界状態にして電気分解を行い、陰極室で生じた亜臨界状態又は超臨界状態の水素ガスとを含む水の圧力又は温度のいずれか一方又は双方を低下させることにより高圧の水素ガスを取出すようにしたので、電極表面で発生する水素ガスの気泡量及び電解液中で発生する水素ガスの気泡量が低下し、液抵抗が抑制される。また従来法のように多量の電解質を加えることなく、電解効率を向上させることができる。また電解後に特別の加圧手段を設けることなく、高圧の水素ガスが得られる。

【図面の簡単な説明】

【図１】本発明の高圧水素ガスの製造装置の構成図。

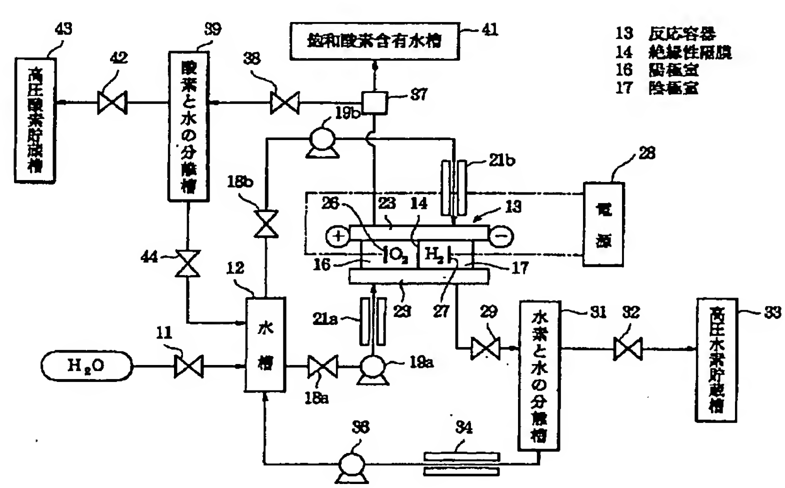
【符号の説明】

１４　絶縁性隔膜

１６　陽極室

１７　陰極室

【図１】



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